

Coplanar and collinear quantum mechanical reactive scattering: The importance of virtual vibrational channels in the $\text{H} + \text{H}_2$ exchange reaction*

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We have performed accurate quantum mechanical calculations for the coplanar $\text{H} + \text{H}_2$ exchange reaction, using sufficient rotational and vibrational basis functions in the close-coupling expansion to ensure convergence. We repeated these calculations with a converged rotational basis set but with only one vibrational basis function, in analogy to what Saxon and Light¹ and Wolken and Karplus,² respectively, did for the similar coplanar and three dimensional reaction. The vibrationally converged and one-vibration results differ substantially for the coplanar as well as the collinear reaction, indicating the crucial role played by virtual vibrational channels.

To solve the Schrödinger equation for the coplanar reaction, we first integrated the appropriate coupled equations into the interaction region from each of the three arrangement channel regions, using an extension of the method developed by Kuppermann.³ The resulting solutions were then smoothly matched on three conveniently chosen surfaces in configuration space. The \mathbf{R} matrix and other asymptotic quantities were then obtained.

Calculations for the Porter-Karplus surface⁴ using 4 or 5 vibrations and 10 or 12 rotations per vibration for a total of 40 to 60 channels yielded reaction probabilities that change by less than 2%–5% as additional vibrational or rotational basis functions are added, over the total energy range 0.30–0.60 eV. Without forcing orthogonalization at any time, the results satisfy conservation of flux to 0.5% or better and time reversal invariance to 6% or better. The calculations were repeated using the same number of rotations but only one vibration, and introducing an appropriate vibrational orthogonalization.

The resulting total reaction cross sections σ_0^R are plotted in Figs. 1(a) and 1(b) and show differences between the vibrationally converged and one-vibration results greater than 3 orders of magnitude at low energies. The ratio of the one-vibration to vibrationally converged ortho-para rate constants is 3.15 at 300 °K and 532 at 100 °K.

Using the method developed previously,³ we calculated the collinear converged⁵ and one-vibration reaction probabilities for the same potential energy surface. The ratios of the coplanar to collinear cross sections are plotted in Fig. 1(c). Although these cross sections vary individually by about 12 orders of magnitude over the energy range considered, their ratios vary by less than 2 orders of magnitude, indicating a remarkably similar energy dependence. Virtual vibrational channels are

furthermore about equally important in the collinear⁶ and coplanar $\text{H} + \text{H}_2$ reaction. This will probably still be the case for this system in three dimensions as well as for other reactions.

We have also calculated the reactive, inelastic, and antisymmetrized differential cross sections for coplanar

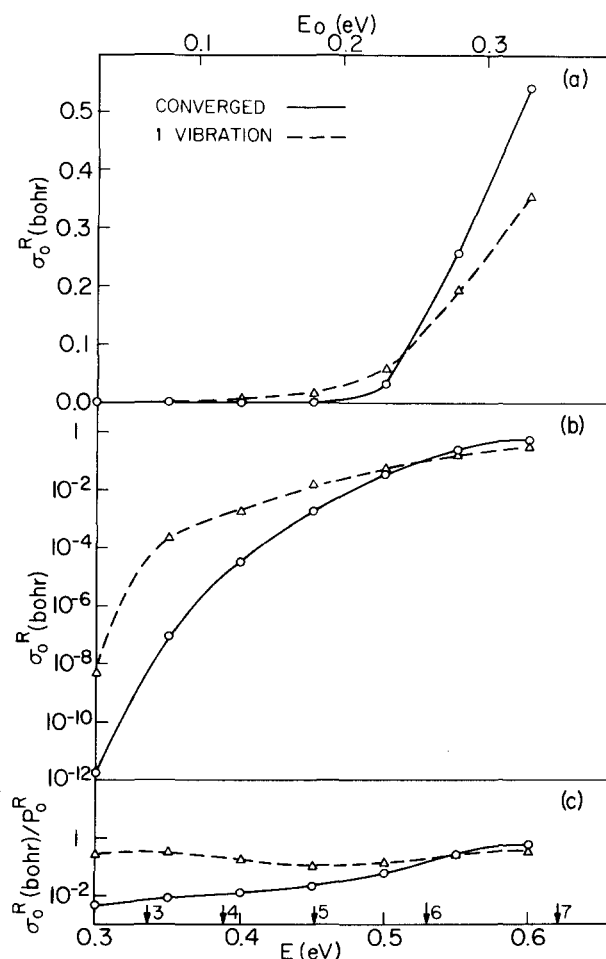


FIG. 1. Total reactive cross section σ_0^R versus the total energy E and translational energy E_0 for the coplanar exchange reaction $\text{H} + \text{H}_2$ ($\nu=0, j=0$) \rightarrow H_2 ($\nu=0, j'$) + H (summed over all j') where the atoms are considered distinguishable. Arrows in abscissa indicate energies at which the vibration-rotation states ($\nu=0, j'$) of H_2 become accessible. (a) Linear plot; (b) semi-logarithmic plot. In (c) we plot the ratio σ_0^R/P_0^R versus energy, where P_0^R is the collinear total reaction probability (the collinear total reaction cross section) for reagents H_2 in $\nu=0$ initially. In all cases, a solid line indicates vibrationally converged results, while a dashed line indicates one-vibration results as defined in text.

$H + H_2$. Contrary to the results of Saxon and Light¹ our reactive differential cross sections show only backward peaking in both the one-vibration and vibrationally converged results. In addition, we find no evidence for a quasiselection rule governing the reaction probabilities similar to the ortho-ortho and para-para nonreactive selection rule. We were able to artificially produce such a reactive quasiselection rule using matching procedures in which incorrect symmetry restrictions were placed on the matched wavefunctions.⁷

The inelastic cross sections are generally backward or sideward peaked and exhibit no fine oscillatory structure. Quantum symmetry oscillations resulting from interference between the direct and exchange amplitudes characterize some ortho-ortho and para-para antisymmetrized differential cross sections at total energies greater than 0.5 eV.

In conclusion, virtual vibrational channels play a central role in the collinear and coplanar $H + H_2$ reaction, and probably in the three dimensional one and in many other reactions. Therefore, the results of calculations using only open vibrational channels must be used with great caution. Once those virtual channels are included in a close-coupling reactive scattering calculation and convergence ascertained, a wealth of detailed physically meaningful information is obtained against which a variety of dynamical models can be tested. Work along these lines is proceeding in this laboratory.

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computational facilities in most of the calculations reported here.

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⁶Virtual channels have been found to be important in many collinear collisions, such as in M. E. Riley and A. Kuppermann, *Chem. Phys. Lett.* 1, 537 (1968); D. G. Truhlar and A. Kuppermann, *J. Chem. Phys.* 52, 3841 (1970); 56, 2232 (1972); S. F. Wu and R. D. Levine, *Mol. Phys.* 22, 881 (1971); and Ref. 3 above.

⁷Recently J. C. Light has obtained similar results in a modified version of his one-vibration method (private communication).

Laser spectroscopy of supersonic molecular beams: Application to the NO_2 spectrum

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Traditional high resolution optical spectroscopy of the type discussed in Herzberg's classic works¹ has been a definitive source of information about the excited electronic states of small molecules. Because the complication caused by rotational structure increases rapidly with increasing molecular weight, high resolution optical studies have been limited to diatomic and reasonably small polyatomic molecules as may be seen in Tables 61-82 of Volume III, Ref. 1. The technique of matrix isolation²⁻⁴ eliminates rotational structure and thus allows work on larger molecules, and on the whole this technique has been highly successful. Unfortunately, matrix isolation spectroscopy suffers from two fundamental problems. First, the matrix completely removes the rotational structure and therefore all information carried by it is lost. Second, the spectrum is perturbed by the matrix, and it is sometimes not clear whether a structural feature deduced from the spectrum

is characteristic of the free molecule or is induced by the matrix.

In this paper we describe an experiment using a supersonic molecular beam⁵⁻⁷ which provides a great reduction in rotational structure without completely removing it, and which allows high resolution study of free molecules unperturbed even by gas phase collisions. In this experiment, a supersonic beam of 5% NO_2 in Ar was crossed with a tunable dye laser beam and the fluorescence excitation spectrum was observed. Because of rotational cooling during the supersonic expansion, the highly complicated and largely unassigned absorption spectrum of NO_2 has been simplified to the point where individual vibronic bands are well separated and a complete rovibronic assignment now appears to be within reach.

The molecular beam source⁸⁻¹⁰ had a 0.05 mm nozzle